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STRUCTURE DETERMINATION OF CROSSPOLYMERIZED POLY (1, 11 - DODEC--ETC(U)
MAY 81 J B LANDO, M THAKUR

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STRUCTURE DETERMINATION OF CROSSPOLYMERIZED
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Electron diffraction patterns were obtained from crosspolymerized crystals of poly (1,11-dodecadiyne), formed by casting thin (>200A) films of uncross-polymerized polymer from chloroform. Two orientations of these crystals were obtained by varying the evaporation rate of the chloroform solvent. Crosspolymerization resulted from subsequent exposure of these samples to Co ⁶⁰ radiation. Thirty-six independent reflections were obtained from the a*c* reciprocal lattice net and a lattice net having b* and the (h 0 h) reciprocal		

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lattice direction as orthogonal axes. Refinement of the structure was accomplished with these data. The unit cell of the crosspolymerized material was monoclinic, space group $P2_1/n$, $a = 9.17\text{\AA}$, b (hydrocarbon chain axis and unique axis) $= 12.15\text{\AA}$, c (polydiacetylene axis) $= 9.92\text{\AA}$ and the angle $\beta = 123.5^\circ$.
↑
data

INTRODUCTION

The crosspolymerization of the macromonomer poly (1, 11 - dodecadiyne), using UV, x-ray or Co⁶⁰ γ-radiation has recently been reported⁽¹⁾.

The term macromonomer is used to describe the original polymer which has a chemical repeat unit $\{(\text{CH}_2)_8\text{-C}\equiv\text{C-C}\equiv\text{C}\}$. The term crosspolymerization is utilized to distinguish systematic polymerization of the diacetylene units to a crystalline structure composed of sheets, as indicated in Fig. 1, from the more familiar random crosslinking that many polymers undergo when exposed to radiation. The crystal structure of the crosspolymerized material was refined using electron diffraction data because of the limited information obtained from x-ray fiber patterns.

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EXPERIMENTAL SECTION:

The macromonomer was prepared by oxidative coupling of $\text{HC}\equiv\text{C} - (\text{CH}_2)_8 - \text{C}\equiv\text{CH}$ using copper-pyridiene catalyst.^{1,2,3} After purification¹ the polymer was dissolved in chloroform to make a dilute solution. A drop of this solution at 4°C, on a carbon coated copper grid, was evaporated to obtain single crystals. These crystals were then irradiated by γ -radiation (100 M rad) for complete crosspolymerization. Diffraction patterns were obtained by a JEOL JEM 100 B electron microscope at 100 KV. A second orientation of the crystals was obtained by casting a film at room temperature. Electron diffraction data were obtained at low beam intensity. The intensity data were collected using a high precision photodensitometer. The peaks in the intensity spectra were quite sharp; therefore the peak heights were taken as the relative intensities of the diffraction maxima. The structure was refined using the 'Lals Mark Six' program originally developed by Arnott and co-workers.⁴

Measurements of the thickness of the crystals was performed in the following way. The crystals on the carbon coated copper grid were carbonshadowed at an angle of 45°. Some part of the substrate remains unexposed to this shadowing due to the height of the crystal which blocks the carbon particles. The unexposed strip manifests itself as a light strip at the edge of the crystal on the electron micrograph. Since the shadowing angle is 45° the width of this strip is the thickness of the crystal.

RESULTS AND DISCUSSION:

The diffraction pattern of the a^*c^* reciprocal lattice net remained sharp for about 20 secs but that of $b^*(h0\bar{h})$ net (rapid evaporation) remained reasonably sharp for only about 13 secs even under the lowest possible beam-intensity. In spite of this we obtained a reasonable number of reflections by developing the pictures appropriately. Initially only the a^*c^* data were used for refinement of the structure. Afterwards the full data were utilized. The equatorial $h0\bar{h}$ reflections, which appeared on both patterns, were used for scaling. The a^*c^* pattern showed a c-axis repeat distance of 9.92\AA which is approximately twice the ideal polydiacetylene chain repeat. Therefore one can safely assume that the diacetylene chain is along the c-axis. The $(h0\bar{h})$ pattern as well as x-ray studies gave a b-axis of 12.25\AA which obviously fits with the hydrocarbon chain repeat. This axis is orthogonal to the ac plane indicating possible chain folding in the macromonomer. Therefore the unit cell is monoclinic. There is a screw axis along b as demonstrated by the absence of $0k0$ $k = \text{odd}$ reflections. The $h0\bar{l}$ plane contains additional systematic absences, $h+l = \text{odd}$, which indicates a glide plane perpendicular to the b-axis. With this information the space group assigned to this crystal is $P2_1/n$.

With the above information at hand we can conveniently choose our starting model as in Fig. 3. We place the diacetylene chain along the c-axis and the hydrocarbon chain along the b-axis. There are four repeat units per unit cell and an n-glide in the ac plane. Therefore there should be one chain at the center of the unit cell.

A series of models, which were small modifications of our preliminary model, were tried. Initially all these models were tested against contact calculations (van der Waals interaction). All possible combinations of the four chains with regard to their senses (UP or DOWN) were taken into consideration. Orientation of the diacetylene rod with respect to the c-c planer zigzag was varied until contacts were minimized. Both carbon and hydrogen atoms were used for structure factor calculation. Since the measured thickness of the crystals is less than 200\AA , dynamical effects were ignored. Or to be more precise, the contribution of the dynamical effect was considered to be within experimental error. The existence of systematic absences was a strong indication that this was a reasonable assumption.

After exploiting the appropriate options provided by Lals we reached a residual of 0.13. The residual we refined is defined as

$$R = \left\{ \sum_{m=1}^N \Delta F_m^2 / \sum_{m=1}^N F_m^2(\text{obs}) \right\}^{1/2}$$

where $\Delta F_m^2 = |F_m^2(\text{obs}) - F_m^2(\text{cal c})|$.

A comparison of calculated and observed structure factors is given in Table 1.

We kept $W_m = 1$ for all diffraction maxima. The projection on the ac plane (Fig. 4) shows that the diacetylene chains remain in the plane of c-c zigzag, which should be energetically favorable. Two UP and two DOWN chains was found to yield the best residual. A DOWN chain is formed by rotating an UP chain by 180° about the a-axis. The ac projection of the DOWN chain is almost identical with that of the UP chain, although

the two chains are not identical (bc projection, Figure 5). This similarity might mislead one to think that the unit cell should be half of what is given.

Final bond angles, dihedral angles, and the bond lengths of the single, double and triple bonds are given in Table 2. The labels of atoms in Table 2 are identical to those in Figure 5.

Single crystal electron diffraction patterns of the predominantly uncrosslinked macromonomer were obtained using high speed x-ray film under very low beam intensity. The unit cell (Table 3) is monoclinic and larger than that of the crosspolymerized polymer. Macroscopically this kind of contraction was observed when the unreacted macromonomer was crosspolymerized. This kind of behaviour has been observed for some other diacetylene polymerizations as well.⁵ The space group symmetry is unaltered by crosspolymerization. Thus the starting model for refining the macromonomer should not be much different from that of the crosspolymerized one. This work is now under way.

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REFERENCES:

1. Day, D. R.; Lando, J. B., submitted to Journal of Polymer Sci., Polymer letters.
2. Campbell, I and Eglinton, G., "Organic Syntheses, Vol. 45, p. 39.
3. Campbell, I. and Galbraith, A., J. Amer. Chem. Soc., 182, 889 (1959)
4. Campbell, P. J. Smith and Arnott, Struther, Acta Cryst. A34, 3 (1978).
5. Day, David R.; Lando, J. B., Macromolecules, 13, 1483 (1980).

LEGEND

- 1) Model of the Reaction of the Macromonomer.
 - A. Macromonomer
 - B. Crosspolymerized
- 2) Electron Diffraction Pattern (a^*c^* reciprocal lattice net).
- 3) Crosspolymerized Poly (1. 11 - Dodecadiyne), Model Structure
- 4) ac Projection of Final Structure, t, triple bond.
- 5) bc Projection of Final Structure. t, triple bond, d, double bond.

TABLE 1

h	k	l	F - CALC	F - OBS
2	0	0	8099	7386
4	0	0	2369	2161
0	2	0	1532	1587
0	4	0	1202	1487
0	6	0	865	1143
0	8	0	682	887
0	0	2	5109	5188
0	0	4	817	1062
1	0	-1	3031	3357
1	0	1	2575	2734
-1	0	3	3458	3479
-1	0	5	526	671
1	0	3	2357	2614
3	0	1	1052	1318
2	0	2	2345	2136
2	0	-2	5329	5140
-2	0	4	949	1294
1	2	-1	572	763
1	4	-1	493	366
1	6	-1	440	898
3	1	-3	271	234
1	1	-1	249	122
2	1	-2	814	244
-1	2	1	293	548
2	2	-2	539	601
-2	2	2	1063	1221
3	2	-3	976	856
4	2	-4	257	671
4	0	-2	2431	2734
4	0	-4	1091	1245
3	0	-3	2864	3113
5	0	-5	1554	1659
5	0	-3	1293	1525

Table 2 continued

h	k	l	F - CALC	F - OBS
-3	0	5	943	1318
3	0	-1	1430	1807
6	0	-4	711	793

TABLE 2

Atoms Constructing the angle	Bond Angle	Dihedral Angle
C ⁰ C ¹ C ²	110.5	
C ¹ C ² C ³	109.6	179.3
C ² C ³ C ⁴	108.8	180.0
C ³ C ⁴ C ⁵	110.5	180.0
C ⁴ C ⁵ C ⁶	112.3	180.0
C ⁵ C ⁶ C ⁷	112.5	180.0
C ⁶ C ⁷ C ⁸	112.5	180.0
C ⁷ C ⁸ C ⁹	108.5	180.0
C ⁸ C ⁹ C ¹⁰	112.0	180.0
C ³ C ⁴ C ¹¹	124.0	356.1
C ⁴ C ¹¹ C ¹²	180.0	358.2
C ⁴ C ⁵ H ^{5A}	110.0	60.0
C ⁴ C ⁵ H ^{5B}	112.1	302.5
C ⁵ C ⁶ H ^{6A}	107.4	60.9
C ⁵ C ⁶ H ^{6B}	106.6	300.0
C ⁶ C ⁷ H ^{7A}	105.9	60.0
C ⁶ C ⁷ H ^{7B}	106.4	300.0
C ⁷ C ⁸ H ^{8A}	113.6	60.0
C ⁷ C ⁸ H ^{8B}	113.2	301.2
C ⁸ C ⁹ H ^{9A}	106.1	61.2
C ³ C ⁹ H ^{9B}	106.5	300.0
C ⁹ C ¹⁰ H ^{10A}	104.5	60.0
C ⁹ C ¹⁰ H ^{10B}	106.8	300.0
C ³ C ² H ^{2A}	105.3	61.4
C ³ C ² H ^{2B}	107.9	298.5
C ² C ¹ H ^{1A}	110.8	60.0
C ² C ¹ H ^{1B}	111.2	300.0

Table 2 continued

-10-

Atoms Constructing the angle	Bond Angle	Dihedral Angle
C ¹ C ⁰ H ^{0A}	106.4	60.0
C ¹ C ⁰ H ^{0B}	107.6	300.0

	C-C	C = C	C≡C	C - H
Bond length (Å)	1.534	1.33	1.20	1.065
(Not refined)				

TABLE 3

Cell Parameters	Macromonomer (unreacted)	Crosspolymerized Material
a	13.25\AA	9.17\AA
b	14.15\AA	12.25\AA
c	7.63\AA	9.92\AA
β	118.5°	123.5°

Unit cell data

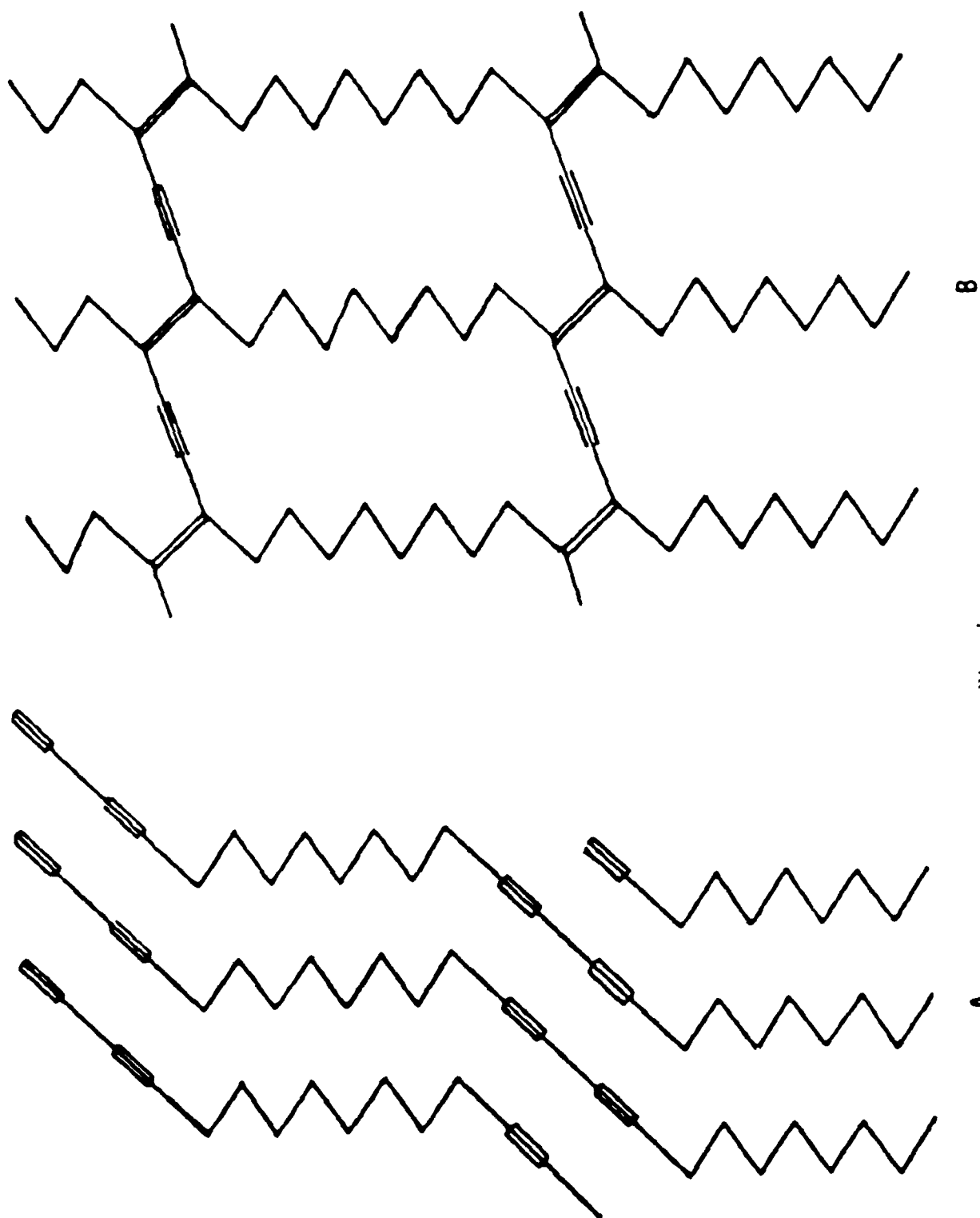


Fig. 1



Fig. 2

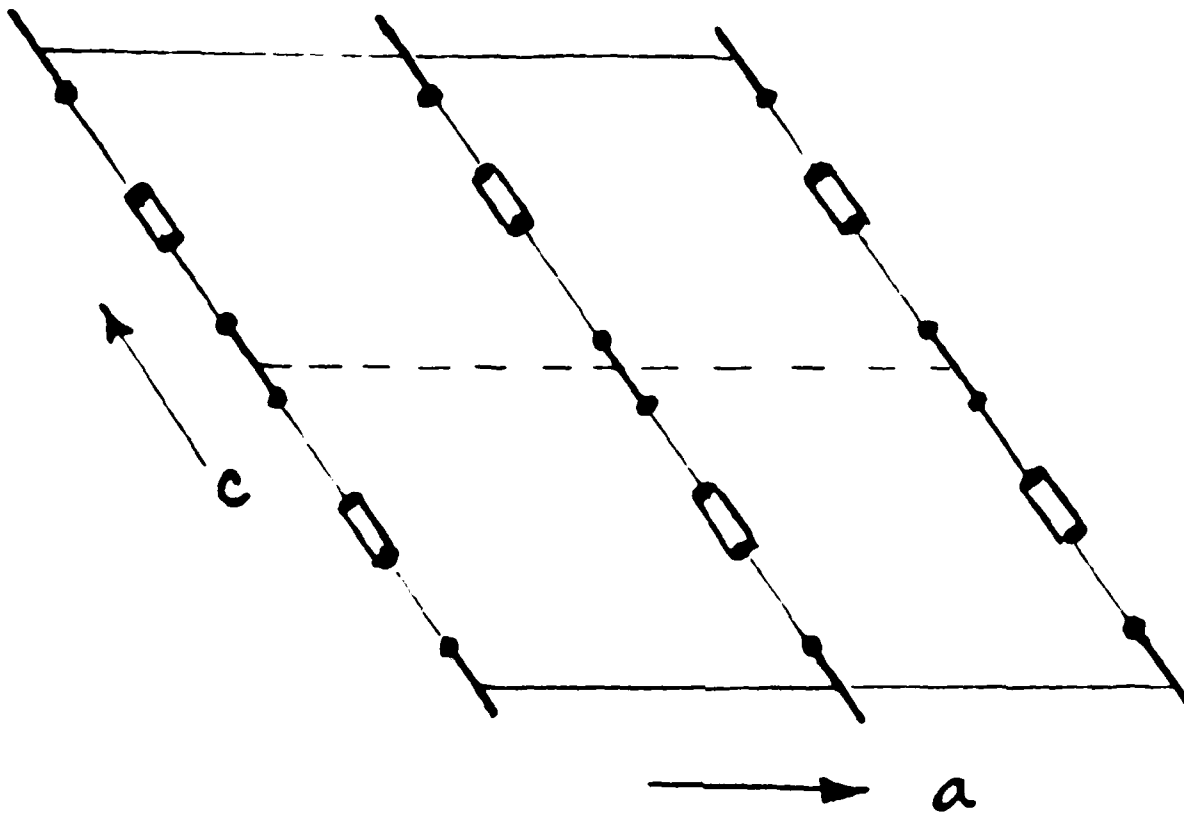


Fig. 3

$a = 9.17 \text{ \AA}$
 $b = 12.25 \text{ \AA}$
 $c = 9.92 \text{ \AA}$
 $\beta = 123.5^\circ$

ac Projection

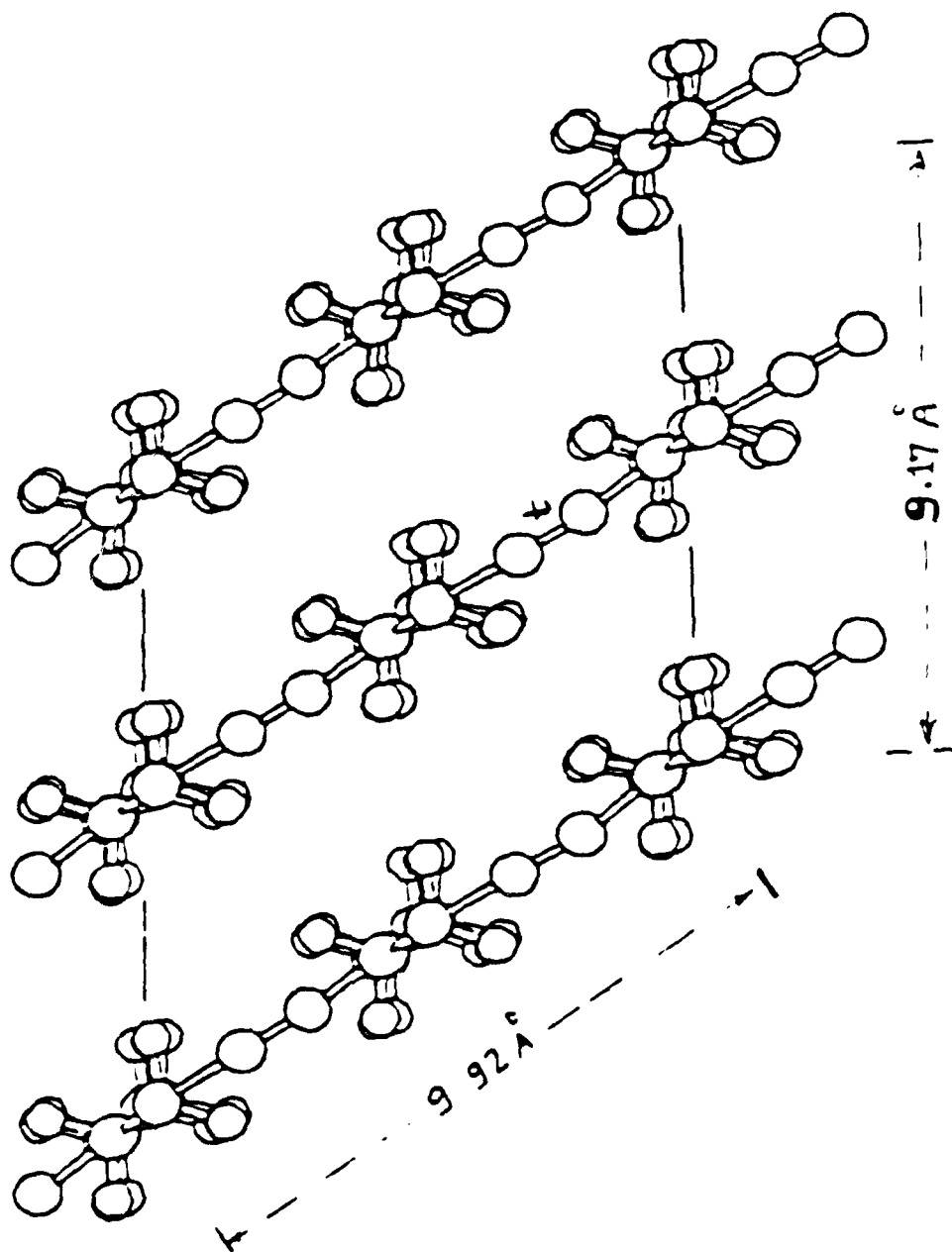


Fig. 4

bc Projection

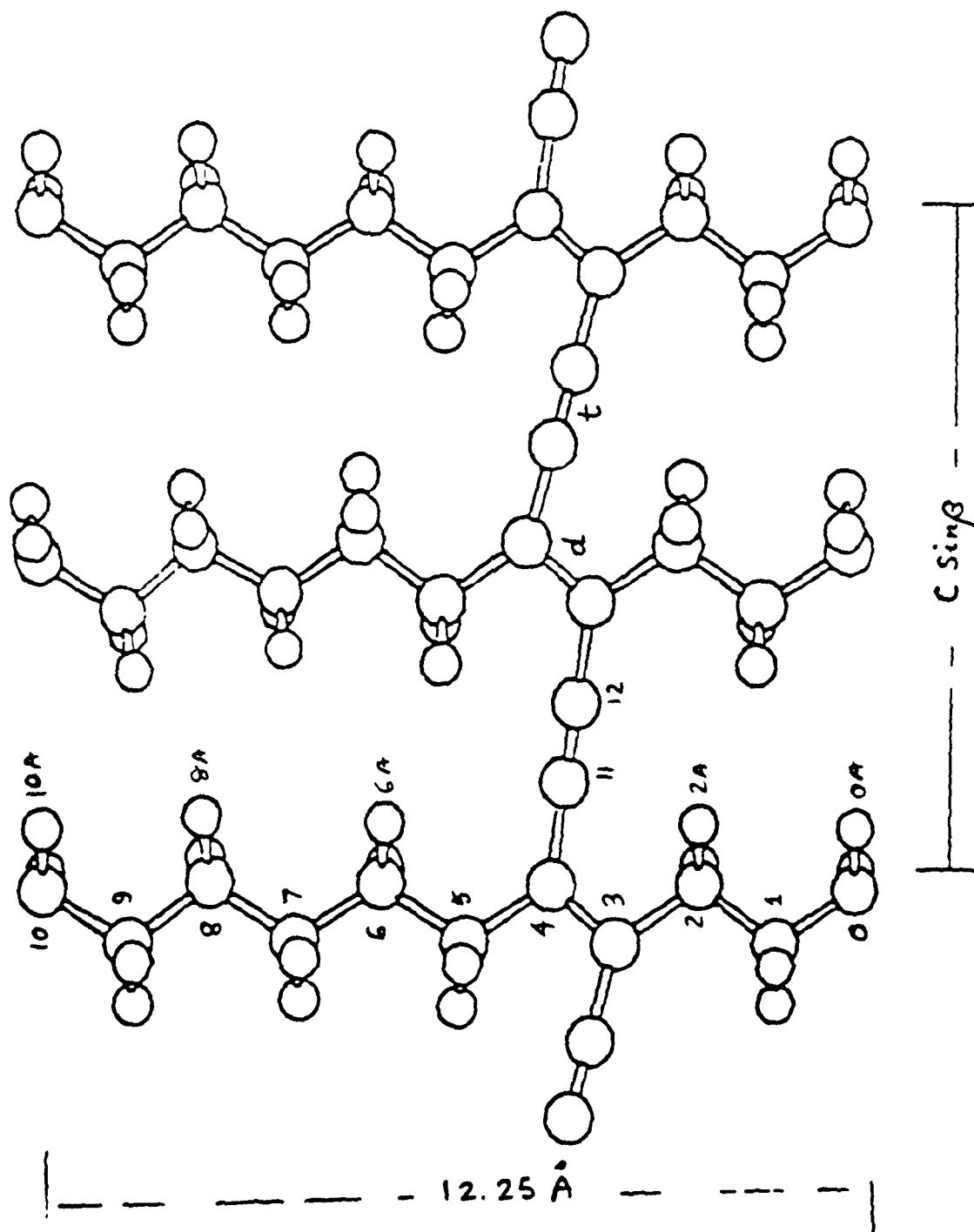


Fig. 5

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